

of durability, they are used in barn and freight-car paints. Synthetic pigment is made by heating iron sulfate. Venetian red is a mixture of ferric oxide with up to an equal amount of the pigment extender, calcium sulfate. This pigment is manufactured by heating ferrous sulfate with quicklime in a furnace. Venetian red is a permanent and inert pigment, particularly on wood. The calcium sulfate content, which furnishes corrosion-stimulating sulfate ions, disqualifies this pigment for use on iron. Indian red is a naturally occurring mineral whose ferric oxide content may vary from 80 to 95%, the remainder being clay and silica. It is made by grinding hematite and floating off the fines for use. *Magnetic* iron oxides have acquired a new market in the production of magnetic tapes for computers and audio and video recorders. The pigment and colorant market utilizes 48 percent of production and magnetic and electronic applications, 11 percent.¹¹

OTHER REDS. *Basic lead chromate* $\text{PbCrO}_4 \cdot \text{Pb(OH)}_2$ may also be used as an orange-red pigment; it is an excellent corrosion inhibitor. It is manufactured by boiling white lead with a solution of sodium dichromate. *Cadmium reds* are made by roasting the precipitate obtained by mixing cadmium sulfate, sodium sulfite, and sodium selenide. Cadmium colors range from light yellow to maroon and are available in pure form as well as in lithopones. The larger the quantity of selenium used, the greater the shift toward red. Red pigments include a large variety of insoluble organic dyes, either in the pure state as toners or precipitated on inorganic bases as lakes. For example *tuscan red* is a name sometimes applied to combinations of red iron oxide pigment and a light-fast organic red pigment used where bright colors are needed for exterior paints. Quinacridones are extremely durable reds, oranges, and violets comparable in serviceability to phthalocyanines.

Yellow Pigments

OCHEER. Ocher is a naturally occurring pigment consisting of clay colored with 10 to 30% ferric hydroxide. It must be ground and levigated. At best the ochers are very weak tinting colors and are being replaced by synthetic hydrated yellow iron oxides for brighter color and better uniformity.

CHROME YELLOWS. Yellow pigments with a wide variety of shades fall in the class known as chrome yellows; they are the most popular yellow pigments because of exceptional brilliance, great opacity, and excellent lightfastness. They are produced by mixing a solution of lead nitrate or acetate with a solution of sodium dichromate. Extenders may be present in up to an equal weight of gypsum, clay, or barite. The pigment is of high specific gravity and settles out. The use of chrome pigments is sharply limited by their toxicity when ingested.

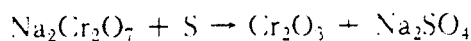
ZINC YELLOW. Zinc yellow or chromate, although of poor tinting power, is used because of its excellent corrosion-inhibiting effect both in mixed paints and as a priming coat for steel and aluminum. Zinc yellow is a complex of the approximate composition $4\text{ZnO} \cdot \text{K}_2\text{O} \cdot 4\text{CrO}_3 \cdot 3\text{H}_2\text{O}$. Two other yellow chromate pigments are strontium chromate and barium chromate, both used as corrosion inhibitors.

¹¹Brown, Iron Oxide, *Chem. Bus.* June 1, 1981, p. 33.

Green Pigments

PHTHALOCYANINE GREEN. The major green pigment is phthalocyanine green. It is a complex copper compound and has excellent opacity, lightfastness, and chemical resistance. It is suitable for use in both solvent- and water-based paints.

CHROMIUM OXIDE GREEN. One of the oldest green pigments is chromium oxide (Cr_2O_3). It has many disadvantages, such as high cost and lack of brilliancy and opacity. It is made by calcining either sodium or potassium dichromate with sulfur in a reverberatory furnace:



GUIGNET'S GREEN. Guignet's green (emerald green) is a hydrated chromic oxide ($\text{Cr}_2\text{O}(\text{OH})_4$), possessing a much more brilliant green color than the oxide and yet having a good permanency. It is prepared by roasting a mixture of sodium dichromate and boric acid at a dull red heat for several hours. In addition, a green of good permanency for use in outside trim paints may be obtained in intimate mixtures of copper phthalocyanine with zinc chromate or hansa yellow. The brightest permanent green available, chlorinated copper phthalocyanine, is expensive but durable. Water-dispersible grades and pulp colors are available for latex paints.

CHROME GREEN. This pigment is sold under various names and is a mixture or a coprecipitation of chrome yellow and prussian blue. Inert fillers are used with this pigment in making paints. Unless carefully ground or coprecipitated, the two colors may separate when mixed in a paint. Also, because of its lead content, it is being phased out of use. It has poor alkali resistance and cannot be used in latex paints.

Brown Pigments

The carefully controlled heating of various naturally occurring iron-containing clays furnishes the brown pigments known as *burnt sienna*, *burnt umber*, and *burnt ocher*. The iron hydroxides are more or less converted to the oxides. The umbers contain brown manganic oxide as well as the iron oxides. These are all permanent pigments suitable for both wood and iron; however, the siennas are being replaced as tinting colors by synthetic oxides because of the latter's greater color strength and clarity. *Vandyke brown* is a native earth pigment of indefinite composition, containing oxide of iron and organic matter.

Toners and Lakes

Toners are insoluble organic dyes that may be used directly as pigments because of their durability and coloring power. Lakes result from the precipitation of organic colors, usually of synthetic origin, upon some inorganic base. They are employed in many colors. Some typical examples are: para red is formed by diazotizing *p*-nitroaniline and coupling it with β -naphthol. Toluidine toner, a better and more expensive red pigment, is made by diazotizing *m*-nitro-*p*-toluidine and coupling it with β -naphthol. Hansa yellow G (lemon yellow) is manufactured by diazotizing *m*-nitro-*p*-toluidine and coupling it with acetoacetanilide. Hansa

yellow 10G (primrose yellow) is made by coupling orthochloroacetanilide with diazotized 4-chloro-2-nitroaniline. Lakes are really dyed inorganic pigments. The inorganic part, or base, consists of an extender such as clay, barite, or blanc fixe and aluminum hydroxide. Either the organic dye may be precipitated onto an already existing base, such as clay or barite suspended in solution, or both the dye and the base may be coprecipitated, e.g., onto blanc fixe or aluminum hydroxide. Both toners and lakes are ground in oil or applied like any other pigment.

Miscellaneous Pigments

In surface coatings, metallic powders, i.e., flaked or finely powdered metals and alloys, have been developed not only for decorative purposes, but also for their durability, heat-reflective properties, and anticorrosion effects. Aluminum flaked powder is usually made by steel-ball milling the granular form in a cylindrical mill to which are added a lubricant and a dispersing agent. Powdered zinc, more often referred to as zinc dust, is used in primers, in paints for galvanized iron, and in finish coats. Lead powders and pastes are used in primers. Though not classed with pigments, one of the uses of metallic stearates is as a pigment-suspending agent. Luminescent paints have a variety of uses, particularly in advertising displays and for aircraft, because of their high visibility.

VARNISHES

A varnish is an unpigmented colloidal dispersion or solution of synthetic and/or natural resins in oils and/or thinners used as a protective and/or decorative coating for various surfaces and which dries by evaporation, oxidation, and polymerization of portions of its constituents. Not being pigmented, varnishes are less resistant to damage by light than are paints, enamels, and pigmented lacquers. They furnish, however, a transparent film, which accentuates the texture of the surface coated. Varnishes are frequently oleoresinous; there are two minor classes, spirit varnishes and japans. Oleoresinous varnishes are solutions of one or more natural or synthetic resins in a drying oil and a volatile solvent. The oil reduces the natural brittleness of the pure-resin film. Spirit varnishes are solutions of resins, but the solvent is completely volatile and nonfilm-forming. Oleoresinous varnishes were formerly of major importance, but alkyd and urethane varnishes have largely replaced them because of greater durability, less yellowing, ease of application, and beauty. Pressure to reduce the amount of air-polluting solvents in varnishes and paints, coupled with the desire for water cleanup of tools and spills, has led to the development of water-thinned varnishes.

Spirit varnishes are solutions of resins in volatile solvents only, such as methanol, alcohol, hydrocarbons, ketones, and the like. Spirit varnishes dry most rapidly but are likely to be brittle and eventually crack and peel off unless suitable plasticizers are added. The preparation of these products involves active stirring, and sometimes heating, to bring about the desired solution. An important example of a spirit varnish is shellac or a solution of the resin shellac in methanol or alcohol. Japans are rarely used now. They are opaque varnishes to which asphalt or some similar material has been added for color and luster. They may be subdivided into baking, semibaking, and air-drying japans, according to their method of application.

For exterior use alkyd resins are the more durable vehicles, whereas modified phenolic

varnishes are used for interior finishes. Their composition varies widely, depending upon cost and end use. Some are applied with a brush, and others are sprayed on the surface. When hardened by baking, they are particularly durable. Alkyd-amine resins are used to improve quality.

RESINS. The original resins used were copals, which consisted of fossil gums from various parts of the world. Another natural but present-day resin widely employed is that from the pine tree, or rosin. When a plant exudes these products, they are called balsams and, upon evaporation of the volatile constituents, they yield the resin. Thus the longleaf, yellow, and hard pines of the southern states, under proper incision, yield a balsam which, after distillation, gives turpentine and a residue called rosin. The latter product is essentially abietic acid (Chap. 32). Most of the natural resins employed are fossil resins that have been buried and gradually changed over centuries. From the rosin of the present, these resins¹² reach back through dammar, copal, and kauri resins to the oldest of the fossil resins, amber. Some resins like kauri and copal are so ancient that they have changed to insoluble products and must be partly depolymerized by heat before they can be dissolved or blended with the hot oils and other constituents in the varnish kettle. An important present-day resin is shellac, or lac resin. Unlike the others, it is the product of animal life and comes from a parasitic female insect (*Coccus lacca*) which, when feeding upon certain trees in India, secretes a protective exudate that eventually coats the twigs, furnishing stick lac. This is collected and purified to the shellac of commerce by rolling, crushing, separating, washing, and bleaching. See Chap. 34.

Overshadowing these natural products are the more recently introduced synthetic resins (Chap. 34). The ranking of synthetic resins by use in industrial finishes is: alkyds, acrylics, epoxies, nitrocellulose, phenolics, urethanes, and the newer promising but expensive types now used in lesser amounts—siliconized alkyds, polyesters and acrylics, fluoropolymers, and polyimides. Phenolic resins (phenol-formaldehyde) were the first of these to be supplied and are still in wide use since they are very resistant to water and many chemicals. In order to make these materials soluble in the oils and solvents in common use in the varnish industry, it is necessary to modify them. This may be done either by fluxing them with softer materials such as ester gum or by controlling the polymerization reaction by choosing a para-substituted phenol, thus stopping the reaction before a final insoluble, infusible product is obtained.

Alkyd resins are formed by condensing dicarboxylic acids with polyhydric alcohols and are modified with fatty acids to gain solubility. As a constituent of varnishes or enamels, they have the distinctive properties of beauty and flexibility which are retained upon prolonged exposure to weather. With their introduction, the surface-coating industry became synthetic minded. The properties of the alkyd formulation may be modified by the use of different fatty acids or oils of both drying and nondrying types, by the use of pentaerythritol for glycerin, by the use of maleic or other dibasic anhydrides for all or part of the phthalic anhydride, and by modifying with other resins (phenolics, rosin, and the like). As such, they find extremely diversified applications in various coating formulations. They have largely replaced varnishes of the oleoresinous type.

Ester gum, the product of the esterification of the abietic acid or rosin with glycerin, is another important raw material for making varnish. In addition to the coumarone-indene types, urea-formaldehyde types, and melamine-formaldehyde resins, some of the newer resins include acrylics, silicones, and vinyls.

Epoxy resins are now widely used for protective and chemical-resistant coatings but fail to meet the mass production requirements of the furniture industry. Quick-drying urethane

¹²Payne, *Organic Coating Technology*, vol. 1, Wiley, New York, 1955, p. 138.

coatings have recently moved from the specialty finish field into broader markets. Original urethane lacquers had two drawbacks, an isocyanate vapor hazard and a two-pot system; now they may be applied from the can. The new finishes fall into two classes: (1) Isocyanate non-reactive oil-modified urethanes make use of toluene diisocyanate (TDI) in combination with polyols such as glycerin, methyl glucoside, linseed, and soybean oil. Major uses are for exterior wood, such as for siding, shingles, boats, and also for interior floors and furniture. (2) Isocyanate reactive types are made by reacting excess TDI or an aliphatic or cycloaliphatic isocyanate with a hydroxyl-bearing substance to form a prepolymer, which then reacts further with the hydroxyl groups of the polyol (first category) or with moisture (second category) to form the film. The use of aliphatic isocyanates has produced coatings of much greater durability. Synthetic resins have numerous advantages over naturally occurring types, such as superior resistance on exposure to weather and chemicals, the ability to be baked more rapidly at higher temperatures, and higher solid content than nitrocellulose lacquers, making a one-spray operation possible.

LACQUERS

Lacquer is a loosely used term. It refers to a coating composition based on a synthetic, thermoplastic, film-forming material dissolved in organic solvents, which dries primarily by solvent evaporation.¹³ Confusion between lacquers and enamels remains in the public mind, which is not surprising in view of the standard definition of an enamel as a paint characterized by the ability to form an especially smooth film. Clear lacquers, upon addition of pigment, become lacquer enamels, or simply pigmented lacquers. Lacquer use is currently limited to coating furniture. When used to coat automobiles, enamels are habitually referred to as lacquers.

Surface coatings packed in pressurized cans (aerosols) are usually lacquers (clear, colored, or metallic), but vinyl coatings resistant to abrasion, sunlight, and moisture; epoxies, and stainless-steel flakes in vinyl or epoxy designed to prevent corrosion of machinery are available.

INDUSTRIAL COATINGS

Alkyd resins are used extensively in industrial coatings. They are widely compatible with oils and other resins, but their durability and resistance to water, sunlight, and chemicals is inferior to that of phenolics.

Phenolics are used to resist alcohols and food acids, particularly in cans and containers, but their use in varnish has lost out to urethanes and other film formers.

Acrylics, available as thermoplastic and thermosetting types (with mixtures compatible), represent the current optimum combination of price, durability, flexibility, and appearance. They are used in automotive topcoats.¹⁴

Epoxies are used in plants where chemical resistance is essential. They require a curing agent and are expensive. They are used on appliances, as linings, and for prime coats.

¹³ASTM Standards, vol. 28, 1982.

¹⁴Zimmt, Coatings from Acrylic Polymers, *CHEMTECH* 11 (11) 681 (1981); Curing Paints at Room Temperatures, *Chem. Week* 132 (2) 52 (1983).

The urethanes are strongly adherent to metal and resist both chemical attack and abrasion. Their clarity and resistance to weather make them useful for severe industrial service.

Fluoropolymers represent the current maximum in weather resistance. The slick surface and good wear resistance cause them to be used as coatings for snow shovels, saws, aircraft, and chute liners.

Polyimide resins are used to coat special pans and other material that must resist temperatures of 275°C continuously or 450°C maximum briefly.

APPLICATION. Traditional application with a brush is increasingly proving too time-consuming. Dip tanks provide cheap application, but coating is uneven and holidays in the coatings are common. Conventional spray equipment is cheap to own and maintain, but gives uniform results only in the hands of skilled operators and frequently results in highly variable film thickness. Spraying is increasingly coming under fire because of its pollution of the air with both volatile solvents and finely divided solids. Electrostatic spraying, in which the paint droplets are made to carry a charge of one polarity while the object being painted is oppositely charged, sharply reduces waste and gives a uniform coat. Its use is limited to metal objects in spray booths. Coil coating of sheets by passing them through baths, sometimes followed by leveling rollers, is efficient in the use of fluids, but edges are hard to coat properly. Electrodeposition¹⁵ may be used with aqueous dispersions of alkyds, polyesters, epoxies, and acrylics solubilized with alkalies such as diethylamine, ammonium hydroxide, and potassium hydroxide. Great coating uniformity is achieved by anodic or cathodic deposition using voltages of 300 to 450 V. The flow of current automatically stops when a coating of 25 to 40 μm has formed because of the insulating properties of resins. The coated part requires about 30 min at 175°C to produce a cross-linked thermoset polymer film. In anodic coating, iron is dissolved from the metal and thus corrosion starts before the steel is coated. Current practice favors cathodic coating where the metal ions are held back and the positive resin ions deposit on the steel.

Fluidized-bed coating and electrostatic spray coating are used to coat metals with powders which are then fused.¹⁶ These techniques are used with epoxies, vinyls, nylons 11 and 12, polyethylene, polypropylene, chlorinated polyethers, melamines, and, no doubt, several other compounds. Air pollution is avoided, and coating quality is excellent, but color problems and wastage cause trouble.

Electron-beam (EB) radiation curing has been tested and shows promise. EB curing works very fast and requires no heat. Prepolymers are cured by using an accelerator's beam. Coatings of baked quality can be produced over heat-sensitive materials such as wood or plastic.

Autodeposition is a new metal finishing technology which activates chemically rather than electrically. It uses aqueous dispersions of polymer, pigment, and metal activators and is operated at room temperature. A high coating efficiency is claimed for this method, which simultaneously pretreats and coats the metal.¹⁷

¹⁵Roobol, Painting with Electricity, *CHEMTECH* 12 (8) 493 (1982); Springer, Strosberg, and Anderson, Conductivity Control of Cathodic Electrocoating, *J. Coat. Technol.* 54 (689) 57 (1981).

¹⁶Hercules Chem., December 1972, p. 1; Conte, Painting with Polymer Powders, *CHEMTECH* 4 (2) 99 (1974); Powder Paint Gets a Ride on a Pinto, *Chem. Week* 116 (2) 41 (1975).

¹⁷Hall, Autodeposition: A Survey of a New Water-Borned Coating Technology, *J. Coat. Technol.* 52 (663) 72 (1980).

Precoating of metals, such as steel and aluminum strips, before fabrication is now widely practiced in the coating field. Roller coaters are unsurpassed in speed and surface quality for coating either one or both sides of continuous strip stock. Resins used are shown in Table 8.5.

MARINE ANTIFOULING COATINGS¹⁸

The problem of preventing fouling of surfaces exposed to the marine environment has been with human beings since recorded history. Originally tar and pitch coatings and copper sheathing were used; later lead sheathing came into use. With the advent of steel ships, metallic sheathing had to be abandoned because of galvanic corrosion. At present, the use of copper oxide in either an insoluble vinyl resin binder or a soluble vinyl resin-rosin binder is common. These work by slowly releasing the toxic copper oxide, but the toxic action slowly decays because of the presence of hydrogen sulfide in polluted waters which results in inactive copper sulfide being formed. The newest and most promising approach is the use of organotin compounds, either alone or combined with copper oxide. Paints containing tributyl tin oxide and/or tributyl tin fluoride are being used. Tests of coatings of organotin compounds chemically linked to a film-forming polymer are showing increased antifouling activity. These coatings are very slightly water soluble so that a fresh film of biocide is constantly being exposed.

PRINTING INKS AND INDUSTRIAL POLISHES

Printing inks consist of a fine dispersion of pigments or dyes in a vehicle which may be a drying oil with or without natural or synthetic resins and added driers or thinners. Drying oils or petroleum oils and resins are employed, although the newer synthetic resin systems are finding great favor because they are quick-drying and their working properties are excellent.

¹⁸Gitlitz, Recent Developments in Marine Antifouling Coatings, *J. Coat. Technol.* 53 (678) 46 (1981); Coatings Make for Smooth Sailing, *Chem. Week* 125 (4) 42 (1979).

Table 8.5 Industrial Coatings

Industrial Finishes Market	Resins in Industrial Finishes
Appliances	Acrylics
Automotive, marine, and aircraft	Alkyds, acrylics
Containers and closures	Epoxies
Industrial and farm equipment	Fluoropolymers
Maintenance	Nitrocellulose
Metal furniture	Phenolics
Paper and flexible packaging	Polyesters
Sheet, strip, and coil coating	Polyimides
Wood furniture	Polyurethanes
	Polyvinyls
	Siliconized polymers
	Ureas and melamines

Printing inks have a large variety of compositions and wide variations in properties.¹⁹ This is because of the great number of different printing processes and types of papers employed. The expensive new magnetic inks, developed for use in a number of electronic machines, are the keys to one type of data processing system. Inks formulated with luminescent pigments achieve a superbright effect; dyes are melted into the resin and baked and, when hard, the material is easily powdered. Rhodamines, auramines, and thioflavins are the principal dyes used in heat-set inks.

Polymer polishes, which have captured 85 percent of the total polish market, have become increasingly popular both in industrial applications and in the large household field. Present-day polishes of the self-drying water-emulsion type had their start in the leather industry in 1926 and since then have undergone numerous improvements.

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¹⁹Miron, Printing with Polymers, *CHEMTECH* 9 (12):746 (1979); George, The Challenges of the Eighties in Coatings and Graphic Arts, *J. Coat. Technol.* 53:674 (1981).

PART 2

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Chapter 1

Nuclear Industries

In the early years of this century, Wilhelm Ostwald, a famed physical chemist, advanced the hypothesis that energy, not mass, is the fundamental basis of matter. Despite this view, colleges continued to teach conservation of mass along with energy for several decades. Becquerel discovered radioactivity in 1898, and the existence of isotopes was shown around 1900. These findings pointed the way to nuclear processes. Reactions involving atomic nuclei showed that matter could be transformed into energy.¹ Fission of the atom was demonstrated by Fermi, followed by Meitner and Frisch. Fission of uranium into two nearly equal fragments yields a tremendous amount of energy that appears as heat accompanied by the emission of neutrons and gamma rays with the simultaneous disappearance of a corresponding amount of mass in accordance with the well-known Einstein equation $e = mc^2$. These discoveries were put to practical use in the form of a sustained chain reaction under the direction of Fermi at the University of Chicago on December 2, 1942, using a nuclear reactor, or pile, of graphite and uranium with a critical mass of a few tons of extremely pure uranium and uranium dioxide. The extremely pure uranium dioxide used and all the early pure uranium metal were manufactured using an ether extraction purification of uranium nitrate hexahydrate. Such purification of inorganic materials with organic solvents represented a new and extremely effective approach to the manufacture of high-purity inorganic salts.

Controlled fission generates heat which can be used to produce steam to drive prime movers, thus generating electricity. The radiation produced during fission can also be used for the synthesis of various isotopes of elements.

Except for incoming solar energy, all world energy sources are finite and exhaustible, and they are being exhausted. Coal, shale oil, petroleum, lignite, and peat are solar derived, have been stored up over millennia, and are being rapidly used up. Probably oils and coal should be conserved as raw materials for use in the process industries; certainly their use as a fuel is not appropriate nor is it in the best long-term interests of humankind. The broad distribution of uranium (and thorium) suitable for centuries of generation of heat and electricity² is a fortunate circumstance and extends the prospects for comfortable energy-consuming existence well beyond the time when cheap oil and gas have been exhausted. Figure 21.1 shows the uranium cycle.

There is an energy shortage in many localities of the world at present because of the difficulty in obtaining sufficient supplies of fuel, primarily coal, oil, and gas. Temporarily, there exists a surplus of uranium fuel. Energy obtained through nuclear fission can greatly reduce the energy shortage. Over 10 percent of the total power used in the United States is currently nuclear-generated. In some parts of the country (e.g., Chicago), around 90 percent of the electricity used is from nuclear units.

¹Glasstone, *Sourcebook on Atomic Energy*, 3d ed., Van Nostrand, New York, 1967.

²ECT, 3d ed., vol. 16, 1981, p. 138.

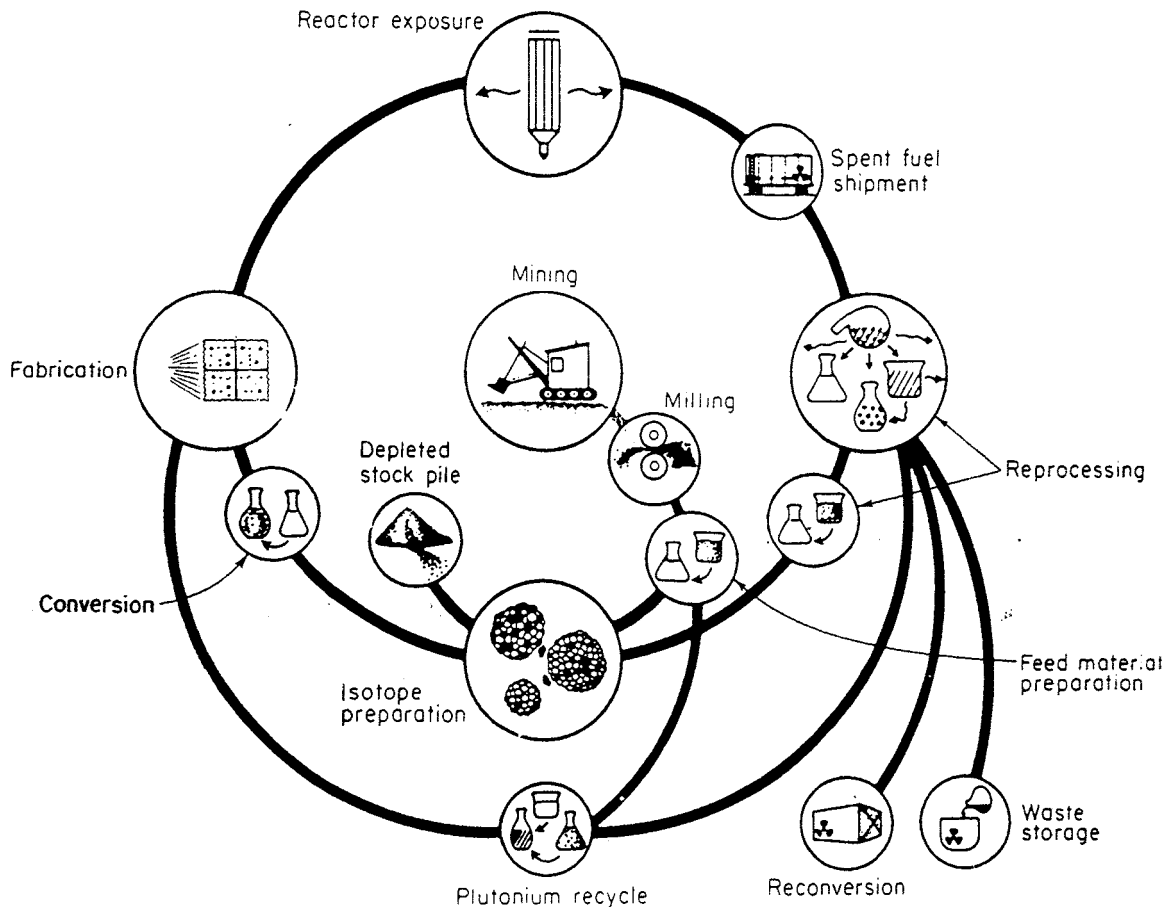


Fig. 21.1. Fuel cycle: from uranium mine through many steps, including plutonium reactor to recycle reconversion and wastes. (R. H. Graham, *World Uranium Reserves and Nuclear Power*.)

In August 1982,³ 274 nuclear units producing 155 GW_e (GW_e = electrical GW) were operating in the world. Of these, 58 percent were pressurized water reactors (PWR), 24 percent boiling water reactors (BWR), 13 percent graphite-moderated, 4.2 percent heavy water-moderated, and 0.6 percent were fast breeder reactors (FBR). Two hundred thirty more units designed to produce 208 GW_e were under construction, and 151 more units to produce 150 GW_e were planned. The later units show increases in the percentage of PWR and FBR with reductions in the other types.

The accident at the Three Mile Island generating plant near Harrisburg, Penn. on March 28, 1979, coupled with a decline in electrical power demand (caused by higher rates and declining business activity) has caused the cancellation or delay of a number of planned nuclear and fossil-fueled plants. The accident also showed the workability of the "defense in depth" safety concept used in all reactors. Although several of the safeguards failed and human response to problems was most erratic, the accident was stopped at a point far short of catastrophe and no one was exposed to significant radiation. Public health hazard was trivial with the statistical probability that radioactive gases released to the atmosphere will cause no more than 0.7 deaths in the next 30 years. Despite this, emotional response to the accident has hampered the expansion of the whole nuclear program.

As each new type of energy has been put at our service, it has encountered public resistance. Coal, steam power, and electrical energy use, for example, have been resisted by pop-

³Power Reactors 1982, a Directory of the World's Power Reactors, *Nucl. Eng. Int.* 27 (330) 2-76, (1982).

list groups claiming "unnaturalness." Nuclear power is encountering such resistance now, and undoubtedly fusion will also be resisted when it develops. Major difficulties have also arisen because of delays in construction combined with high interest rates. Capital costs have skyrocketed, due in part to constantly altered regulations which make for still greater construction delays. Construction workers' productivity has been low. No other chemical process industry endures such pervasive government control.

The dangers of nuclear power use, as seen by some persons, arise to some extent from the destruction observed from the use of the atomic bomb. Such high-power explosions would not occur in the very unlikely case of a major nuclear reactor accident. Inadvertent criticality self-limits at 316 to 31,600 kJ and would not cause a bomb-type explosion.⁴

NUCLEAR REACTIONS

The first spontaneously decaying substances discovered were radium and polonium isolated by the Curies in a marvelous scientific achievement. Nuclear reactor-produced isotopes now replace these substances for industrial and medicinal uses and are far cheaper and safer.⁵

URANIUM AND THORIUM FISSION

Under appropriate conditions, neutrons react with uranium and thorium to produce new isotopes, some stable, others having extremely short half-lives. A ^{235}U atom absorbs a thermal (i.e., relatively slow) neutron, then fissions (splits) into fragments of approximately one-half the original atomic weight, gives up neutrons, and a substantial amount of heat energy.

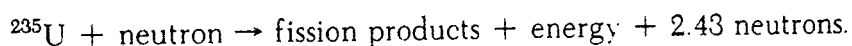


Figure 21.2 shows the range of products formed by the bombardment of ^{235}U with slow and fast neutrons. This is the well-known "camel's hump" curve.

Neutrons released by fission are at high energy levels (fast neutrons) and can react in fast reactors, but most reactors require that they be slowed down to thermal speeds before they can be captured by (i.e., react with) ^{235}U . Slowing down is done by repeated elastic collisions with the so-called moderators, substances such as carbon, H_2O , or D_2O which absorb few neutrons but permit elastic collisions. Of the 2.43 neutrons released, one is needed to continue the chain reaction, and the others may bring about other nuclear reactions or be lost through leakage or capture by elements in the reactor.

Naturally occurring uranium contains only 0.71% ^{235}U , the remainder being ^{238}U . To sustain the chain reaction and obtain usable energy, the ^{235}U content is increased by isotope separation and concentration.

⁴ECT, op. cit.

⁵Benedict, Pigford, and Levi, *Nuclear Chemical Engineering*, 2nd ed., McGraw-Hill, New York, 1982.

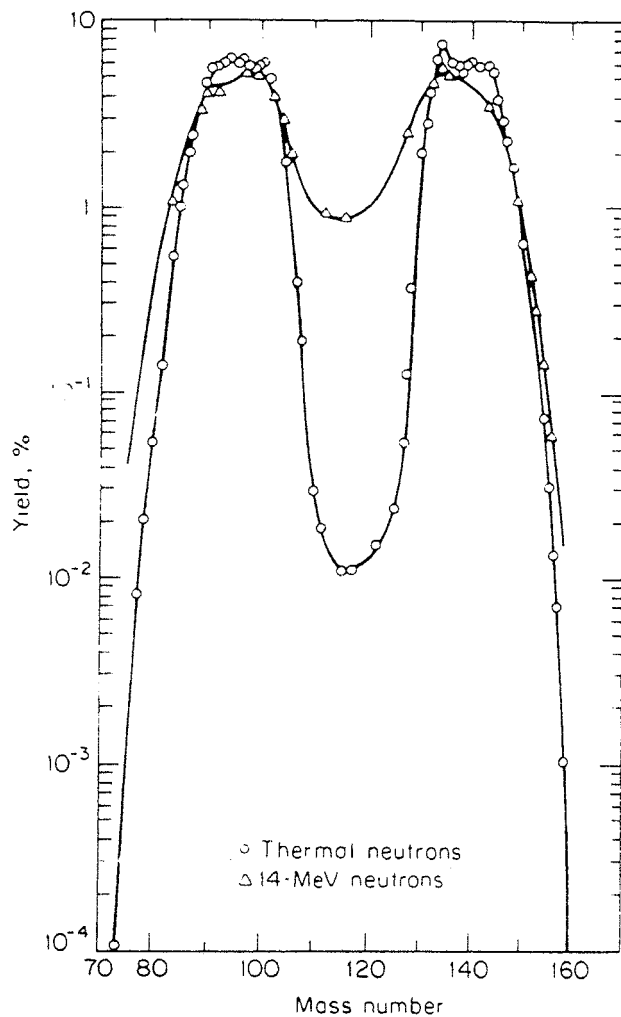
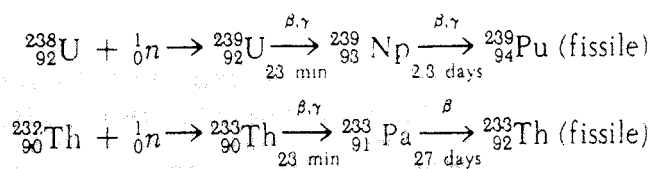


Fig. 21.2. ^{235}U fission product yield against mass number. (ANL 5800.)

Unmoderated natural uranium cannot sustain a chain reaction. Enrichment with ^{235}U reduces reactor size and increases the period between fuel replacements. The common isotopes of uranium and thorium, ^{238}U and ^{232}Th , do not split (fission) on absorbing a neutron, but do form other elements that undergo rapid, spontaneous decay to yield isotopes that are fissionable, so they are usable for power production.

The reactions are:



Isotopes that are not fissile but are convertible to fissile materials are called fertile materials. The synthesis of such elements and other heavier ones, the transuranic elements, on a large scale is an important scientific development. ^{239}Pu has a long half-life (24,000 years) and is quite important because it has a high cross section (ability to absorb) for fast neutrons and a low critical mass for fast fission, desirable properties for military applications. The Savannah River, S.C. plant is the major U.S. manufacturing facility for weapons-grade plutonium. Fuel-grade plutonium is produced as a by-product of water-moderated power reactors.

URANIUM AS AN ENERGY SOURCE

The diminishing availability of reasonably priced fossil fuels has led to conservation practices which have decreased the energy demand. Conservation is certainly desirable. The decreased energy demand and the emotional public outcry against reactors following the Three Mile accident have reduced the demand for uranium as fuel and created a temporary surplus. Capital costs for electrical energy made in nuclear-fueled plants are greater than for traditional fuels, but uranium is the lowest cost fuel available at present and its price has risen at a lower rate than those of other fuels during the last 15 years as shown in Table 21.1. At the present, electricity generated by nuclear plants and that from fossil fuels are virtually identical in total cost.⁶ The greater safety and cleanliness of nuclear units should ultimately make them the more attractive choice.

The current price of uranium (\$70 to \$77 per kilogram in 1982) is depressed by low demand, but with present technology, uranium at \$110 per kilogram is cheaper than residual oil at \$250 per metric ton. A \$1 per kilogram increase in the price of U_3O_8 is equivalent to 10 cents per metric ton increase for coal or 17 cents per metric ton increase for oil. These figures show that as a base load fuel, uranium is clearly cheaper than oil at the present time. Of course, fuel is only one of the major costs involved in power generation. Waste disposal and decommissioning costs have become major considerations. Solid waste disposal costs for coal have been estimated by the General Accounting Office of the U.S. government (in 1980) as costing roughly three times more than that for nuclear waste (coal between 1.0 and 1.2 mills/MJ, nuclear 0.22 to 0.36 mills/MJ). The CO_2 and SO_2 in the gaseous fossil fuel discharge are also objectionable and may ultimately require limitation.

There exists the virtual certainty that demand for uranium will continue and increase. The U.S. known sources of available energy show uranium as the major reserve. See Table 21.2.

Uranium in the United States is found in sandstones of the Colorado plateau, basins in Wyoming, and the gulf coast plains of Texas. It is also present in phosphate rock in Florida and the western states and can be recovered as a by-product of processing for the manufacture of phosphatic fertilizers. By-product concentrations as low as 50 to 130 ppm are workable. Rich ores are present in Canada and Africa. States producing uranium are (in order of production) New Mexico, Wyoming, Texas, Colorado, Florida, Utah, and Washington.

⁶Crowley and Griffith, U.S. Construction Cost Rise Threatens Nuclear Option, *Nucl. Eng. Int.* 27 (238) 25 (1982).

Table 21.1 Cost of Fuel for Electricity Generation, 1965 to 1980 (Fuel cost data in cents per GJ = 10^9 J)

Fuel	1965	1970	1975	1980
Bituminous coal	19.0	26.4	91.8	152.8
Subbituminous coal	11.6	13.7	52.4	120.2
Residual oil	36.9	52.7	212.4	451.3
Natural gas	26.4	28.5	79.5	224.6
Nuclear fuel	21.1	23.2	30.6	39.6

SOURCE: C. M. Valorie, *Power Plant Fuels and Their Effects on the Cost of Electricity*, United Engineers and Constructors.